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(54) Title: MILLIMETER-LONG NANOWIRES

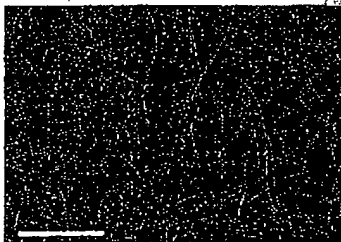


Fig. 1A

(57) Abstract: The present invention generally relates to wires, including nanowires such as semiconductor nanowires, which may be a single crystal in some cases. In one aspect, the present invention is generally directed to a relatively long semiconductor wire. The semiconductor wire may have a length of at least about 10 micrometers, at least about 100 micrometers, or even at least about 1 mm. In certain cases, the semiconductor wire has an aspect ratio of at least about 50,000. In some embodiments, the semiconductor wire has no more than 1 grain boundary per micrometer, and in certain embodiments, the semiconductor wire is a single crystal. In many instances, the semiconductor wire also has a substantially uniform diameter. Other aspects of the invention are directed to techniques for forming such semiconductor wires, e.g., using chemical vapor deposition, as well as devices including such semiconductor wires. For instance, one embodiment of the invention provides an electronic device having at least 50 transistors on a common nanoscale wire.

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MILLIMETER-LONG NANOWIRES**RELATED APPLICATIONS**

This application claims the benefit of U.S. Provisional Patent Application Serial
5 No. 60/860,460, filed November 21, 2006, entitled "Millimeter-Long Nanowires," by
Park, *et al.*, incorporated herein by reference.

FIELD OF INVENTION

The present invention generally relates to nanotechnology and, in particular, to
wires, including nanowires such as semiconductor nanowires.

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BACKGROUND

Interest in nanotechnology, in particular sub-microelectronic technologies such as
semiconductor quantum dots and nanowires, has been motivated by the challenges of
chemistry and physics at the nanoscale, and by the prospect of utilizing these structures
in electronic and related devices. Nanoscopic articles might be well-suited for transport
15 of charge carriers and excitons (e.g. electrons, electron pairs, etc.), and thus may be
useful as building blocks in nanoscale electronics applications.

Semiconducting nanoscale wires are attractive building blocks for fabricating
numerous functional nanodevices, e.g., as discussed in U.S. Patent Application Serial
No. 09/935,776, filed August 22, 2001, entitled "Doped Elongated Semiconductors,
20 Growing Such Semiconductors, Devices Including Such Semiconductors, and
Fabricating Such Devices," by Lieber, *et al.*, published as U.S. Patent Application
Publication No. 2002/0130311 on September 19, 2002; U.S. Patent Application Serial
No. 10/020,004, filed December 11, 2001, entitled "Nanosensors," by Lieber, *et al.*,
published as U.S. Patent Application Publication No. 2002/0117659 on August 29, 2002;
25 or U.S. Patent Application Serial No. 10/196,337, filed July 16, 2002, entitled
"Nanoscale Wires and Related Devices," by Lieber, *et al.*, published as U.S. Patent
Application Publication No. 2003/0089899 on May 15, 2003; each incorporated herein
by reference. Other device elements such as multiplexing biosensor arrays have also
been demonstrated, e.g., in International Patent Application No. PCT/US2005/020974,
30 filed June 15, 2005, entitled "Nanosensors," by Wayne Wang, *et al.*; U.S. Patent
Application Serial No. 11/501,466, filed August 9, 2006, entitled "Nanoscale Sensors,"

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by Lieber, *et al.*; or U.S. Provisional Patent Application Serial No. 60/812,884, filed June 12, 2006, entitled "Nanosensors and Related Technologies," by Lieber, *et al.*; each incorporated herein by reference. However, improvements in nanotechnologies are still needed.

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SUMMARY OF THE INVENTION

The present invention generally relates to wires, including nanowires such as semiconductor nanowires. The subject matter of the present invention involves, in some cases, interrelated products, alternative solutions to a particular problem, and/or a plurality of different uses of one or more systems and/or articles.

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One aspect of the invention is directed to an article. The article, in one set of embodiments, includes a wire, such as a semiconductor wire, having a portion having a length of at least about 0.3 mm and/or a thickness of no more than about 500 nm. In another set of embodiments, the article includes a wire, such as a semiconductor wire, having an aspect ratio of at least about 2000. In some cases, the wire has no more than

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about 1 grain boundary per micrometer.

The article, in yet another set of embodiments, includes at least 50 transistors, diodes, sensors, memories, and/or photovoltaic cells each comprising a common nanoscale wire. In still another set of embodiments, the article includes at least 50 transistors, diodes, sensors, memories, and/or photovoltaic cells each comprising a

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common wire having no more than 1 grain boundary per micrometer of common wire.

Another aspect of the invention is directed to a method. In one set of embodiments, the method includes an act of growing a semiconductor wire from a nanoparticle using chemical vapor deposition by exposing the nanoparticle to Si_2H_6 and/or Ge_2H_6 . In another set of embodiments, the method includes an act of growing a

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wire, such as a semiconductor wire, from a nanoparticle using chemical vapor deposition at a temperature of between about 300 °C and about 500 °C.

In another aspect, the present invention is directed to a method of making one or more of the embodiments described herein, for example, a semiconductor wire having a length of at least 1 mm. In another aspect, the present invention is directed to a method

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of using one or more of the embodiments described herein, for example, a semiconductor wire having a length of at least 1 mm.

Other advantages and novel features of the present invention will become apparent from the following detailed description of various non-limiting embodiments of

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the invention when considered in conjunction with the accompanying figures. In cases where the present specification and a document incorporated by reference include conflicting and/or inconsistent disclosure, the present specification shall control. If two or more documents incorporated by reference include conflicting and/or inconsistent disclosure with respect to each other, then the document having the later effective date shall control.

BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention. In the figures:

Figs. 1A-1C illustrate nanowires according to one embodiment of the invention;

Figs. 2A-2C illustrate structural characteristics of certain nanowires according to another embodiment of the invention;

Figs. 3A-3I illustrate characteristics of certain doped nanowires and devices using such doped nanowires, according to yet another embodiment of the invention; and

Figs. 4A and 4B illustrate a sensor array using certain nanowires of the invention, in still another embodiment of the invention.

DETAILED DESCRIPTION

The present invention generally relates to wires, including nanowires such as semiconductor nanowires, which may be a single crystal in some cases. In one aspect, the present invention is generally directed to a relatively long semiconductor wire. The semiconductor wire may have a length of at least about 10 micrometers, at least about 100 micrometers, or even at least about 1 mm. In certain cases, the semiconductor wire has an aspect ratio of at least about 50,000. In some embodiments, the semiconductor wire has no more than 1 grain boundary per micrometer, and in certain embodiments, the semiconductor wire is a single crystal. In many instances, the semiconductor wire also has a substantially uniform diameter. Other aspects of the invention are directed to techniques for forming such semiconductor wires, e.g., using chemical vapor deposition, as well as devices including such semiconductor wires. For instance, one embodiment of

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the invention provides an electronic device having at least 50 transistors on a common nanoscale wire.

In the discussion below, it should be understood that a description of a wire, such as a nanowire, also includes, besides embodiments having one or more of the features described below, embodiments in which a first portion of a wire has one or more features described below, and other portions of the wire contain other features distinguishable from the first portion (for example one or more of those described below, and/or other features). For example, a nanowire of the invention may contain a longitudinal or a core/shell heterojunction, e.g., as is discussed in U.S. Patent Application Serial No. 10/196,337, filed July 16, 2002, entitled "Nanoscale Wires and Related Devices," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2003/0089899 on May 15, 2003, incorporated herein by reference.

One aspect of the invention is generally directed to relatively long wires, for example comprising a semiconductor, as discussed below. In some cases, the wire has a length of at least about 10 micrometers, at least about 30 micrometers, at least 50 micrometers, at least about 100 micrometers, at least about 300 micrometers, at least 500 micrometers, at least 750 micrometers, or even at least about 1 millimeter. As used herein, a "wire" generally refers to any material having a conductivity of or of similar magnitude to any semiconductor or any metal, and in some cases, may be used to connect two electronic components such that they are in electronic communication with each other. Typically, the wire is solid. The terms "electrically conductive," a "conductor," or an "electrical conductor," when used with reference to a "conducting" wire such as a nanoscale wire, refers to the ability of that wire to pass charge. Typically, an electrically conductive nanoscale wire will have a resistivity comparable to that of metal or semiconductor materials, and in some cases, the electrically conductive nanoscale wire may have lower resistivities, for example, resistivities of less than about 100 microOhm cm ($\mu\Omega$ cm). In some cases, the electrically conductive nanoscale wire will have a resistivity lower than about 10^{-3} ohm meters, lower than about 10^{-4} ohm meters, or lower than about 10^{-6} ohm meters or 10^{-7} ohm meters.

In certain embodiments of the invention, the wire (or at least a portion thereof) is a nanowire. A "nanowire" (e. g. comprising silicon and/or another semiconductor material) is a nanoscopic wire that is typically a solid wire, that at any point along its

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length, has at least one cross-sectional dimension and, in some instances, two orthogonal cross-sectional dimensions that are less than 1 micrometer, less than about 500 nm, less than about 200 nm, less than about 150 nm, less than about 100 nm, less than about 70, less than about 50 nm, less than about 30 nm, less than about 20 nm, less than about 10 nm, or less than about 5 nm. In certain cases, the cross-sectional dimension is less than about 2 nm or about 1 nm. In certain instances, the nanowire has at least one cross-sectional dimension ranging from about 0.5 nm to about 100 nm or about 200 nm. The nanowire is electrically conductive in some cases. The cross-section of a nanowire may be of any arbitrary shape, including, but not limited to, circular, square, rectangular, annular, polygonal, or elliptical, and may be a regular or an irregular shape.

A "width" of an article, as used herein, is the distance of a straight line from a point on a perimeter of the article, through the center of the article, to another point on the perimeter of the article. As used herein, a "width" or a "cross-sectional dimension" at a point along a longitudinal axis of an article is the distance along a straight line that passes through the center of a cross-section of the article at that point and connects two points on the perimeter of the cross-section. The "cross-section" at a point along the longitudinal axis of an article is a plane at that point that crosses the article and is orthogonal to the longitudinal axis of the article. The "longitudinal axis" of an article is the axis along the largest dimension of the article. Similarly, a "longitudinal section" of an article is a portion of the article along the longitudinal axis of the article that can have any length greater than zero and less than or equal to the length of the article. Additionally, the "length" of an elongated article is a distance along the longitudinal axis from end to end of the article.

As used herein, "nanoscopic-scale," "nanoscopic," "nanometer-scale," "nanoscale," the "nano-" prefix (for example, as in "nanostructured"), and the like generally refers to elements or articles having widths or diameters of less than about 1 micron, and less than about 100 nm in some cases. The specified widths can be a smallest width (i.e. a width as specified where, at that location, the article can have a larger width in a different dimension), or a largest width (i.e. where, at that location, the article has a width that is no wider than as specified, but can have a length that is greater).

In some embodiments, a wire of the invention may have a relatively large aspect ratio (length to cross-sectional thickness). For example, the aspect ratio of the wire may

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be at least about 1000:1, at least about 2000:1, at least about 3000:1, at least about 5000:1, at least about 10,000:1, at least about 20,000:1, at least about 30,000:1, at least about 50,000:1, at least about 100,000:1, at least about 200,000:1, at least about 500,000:1, etc.

5 In one set of embodiments, the wire (or portion thereof) is a semiconductor wire, for example, a wire that is formed of silicon and/or other semiconductor materials. In some cases, the semiconductor comprises or consists essentially of silicon, and, as discussed below, in certain instances, the silicon and/or other semiconductor is present as a single crystal. In another embodiment, the semiconductor comprises or consists
10 essentially of germanium. A "semiconductor," as used herein, is given its ordinary meaning in the art, i.e., an element having semiconductive or semi-metallic properties (i.e., between metallic and non-metallic properties). One example of a semiconductor is silicon. Other non-limiting examples include gallium, germanium, diamond (carbon), tin, selenium, tellurium, boron, or phosphorous. Other examples of suitable materials
15 include, but are not limited to, inorganic structures such as main group and metal atom-based wire-like silicon, transition metal-containing wires, gallium arsenide, gallium nitride, indium phosphide, germanium, cadmium selenide, etc.

In some cases, the wire includes additional materials, such as semiconductor materials, dopants, organic compounds, inorganic compounds, etc. The following are
20 non-limiting examples of materials that may be used as dopants within the wire. The dopant may be an elemental semiconductor, for example, silicon, germanium, tin, selenium, tellurium, boron, diamond, or phosphorous. The dopant may also be a solid solution of various elemental semiconductors. Examples include a mixture of boron and carbon, a mixture of boron and P(BP₆), a mixture of boron and silicon, a mixture of
25 silicon and carbon, a mixture of silicon and germanium, a mixture of silicon and tin, a mixture of germanium and tin, etc. In some instances, the dopant may include mixtures of Group IV elements, for example, a mixture of silicon and carbon, or a mixture of silicon and germanium. In some embodiments, the dopant may include mixtures of Group III and Group V elements, for example, BN, BP, BAs, AlN, AlP, AlAs, AlSb,
30 GaN, GaP, GaAs, GaSb, InN, InP, InAs, or InSb. Combinations of these mixtures may also be used, for example, a mixture of BN/BP/BAs, or BN/AlP. In other embodiments, the dopants may include mixtures of Group III and Group V elements. For example, the mixtures may include AlGaIn, GaPAs, InPAs, GaInN, AlGaInN, GaInAsP, or the like.

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In other embodiments, the dopants may also include mixtures of Group II and Group VI elements. For example, the dopant may include mixtures of ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, HgTe, BeS, BeSe, BeTe, MgS, MgSe, or the like. Alloys or mixtures of these dopants are also possible, for example, ZnCdSe, ZnSSe, or the like. Additionally, mixtures of different groups of semiconductors may also be possible, for example, combinations of Group II-Group VI and Group III-Group V elements, such as $(\text{GaAs})_x(\text{ZnS})_{1-x}$. Other non-limiting examples of dopants may include mixtures of Group IV and Group VI elements, for example GeS, GeSe, GeTe, SnS, SnSe, SnTe, PbO, PbS, PbSe, PbTe, etc. Other dopant mixtures may include mixtures of Group I elements and Group VII elements, such as CuF, CuCl, CuBr, CuI, AgF, AgCl, AgBr, AgI, or the like. Other dopant mixtures may include different mixtures of these elements, such as BeSiN_2 , CaCN_2 , ZnGeP_2 , CdSnAs_2 , ZnSnSb_2 , CuGeP_3 , CuSi_2P_3 , Si_3N_4 , Ge_3N_4 , Al_2O_3 , $(\text{Al, Ga, In})_2(\text{S, Se, Te})_3$, Al_2CO , $(\text{Cu, Ag})(\text{Al, Ga, In, Tl, Fe})(\text{S, Se, Te})_2$ or the like.

As a non-limiting example, a p-type dopant may be selected from Group III, and an n-type dopant may be selected from Group V. For instance, a p-type dopant may include at least one of B, Al, and In, and an n-type dopant may include at least one of P, As, and Sb. For Group III-Group V mixtures, a p-type dopant may be selected from Group II, including one or more of Mg, Zn, Cd and Hg, or Group IV, including one or more of C and Si. An n-type dopant may be selected from at least one of Si, Ge, Sn, S, Se, and Te. It will be understood that the invention is not limited to these dopants, but may include other elements, alloys, or mixtures as well.

As used herein, the term "Group," with reference to the Periodic Table, is given its usual definition as understood by one of ordinary skill in the art. For instance, the Group II elements include Mg and Ca, as well as the Group II transition elements, such as Zn, Cd, and Hg. Similarly, the Group III elements include B, Al, Ga, In and Tl; the Group IV elements include C, Si, Ge, Sn, and Pb; the Group V elements include N, P, As, Sb and Bi; and the Group VI elements include O, S, Se, Te and Po. Combinations involving more than one element from each Group are also possible. For example, a Group II-VI material may include at least one element from Group II and at least one element from Group VI, e.g., ZnS, ZnSe, ZnSSe, ZnCdS, CdS, or CdSe. Similarly, a Group III-V material may include at least one element from Group III and at least one element from Group V, for example GaAs, GaP, GaAsP, InAs, InP, AlGaAs, or InAsP.

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Other dopants may also be included with these materials and combinations thereof, for example, transition metals such as Fe, Co, Te, Au, and the like. The nanoscale wire of the present invention may further include, in some cases, any organic or inorganic molecules. In some cases, the organic or inorganic molecules are polarizable and/or have multiple charge states.

In certain embodiments of the invention, the wire, or at least a portion thereof, has a substantially uniform diameter. For example, the diameter of the wire may have a maximum variation of no more than about 100%, about 75%, about 50%, about 25%, about 20%, about 15%, about 10%, or about 5%, relative to the average diameter of the wire. In certain cases, the relative variation may be no more than about 100 nanometers, about 50 nanometers, about 30 nanometers, about 20 nanometers, about 10 nanometers, about 5 nanometers, about 3 nanometers, about 2 nanometers, about 1 nanometer, etc., relative to the average diameter of the wire. The average diameter of the wire is the average cross-sectional dimension of the wire, averaged over the entire length of the wire. In some cases, the maximum variation may be expressed as a ratio of the variation relative to the average diameter of the wire, divided by the length of the wire. Wires of the invention may have, in certain instances, ratios of less than about 0.1, less than about 0.05, less than about 0.03, less than about 0.01, less than about 0.005, less than about 0.003, or less than about 0.001.

A wire (or at least a portion thereof), in some embodiments of the invention, has one, or a relatively small number of crystals. For example, the wire may have no more than about one grain boundary per 10 micrometers of wire, per 100 micrometers of wire, or no grain boundaries may be present, i.e., the wire is a single crystal. As used herein, a "single crystal" item is a crystal that has covalent bonding, ionic bonding, or a combination thereof throughout the crystal. Such a single crystal item may include defects in the crystal, but is distinguished from an item that includes one or more crystals, not ionically or covalently bonded, but merely in close proximity to one another. Crystals that are adjacent each other, e.g., along a wire, are often separated by grain boundaries. A grain boundary generally is the interface between two (or more) crystals in a polycrystalline material. Grain boundaries can be determined, for example, with transmission electron microscopy (TEM), using no more than routine skill.

Another aspect of the invention is generally directed to systems and methods for producing wires and nanowires such as those described above. In one set of

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embodiments, VLS (vapor-liquid-solid) processes may be used to produce the wire (or portion thereof), for example, with techniques such as laser-assisted catalytic growth (LCG). For example, wires such as Si nanowires may be synthesized using laser assisted catalytic growth (LCG). In LCG, laser vaporization of a composite target that is
5 composed of a desired material (e.g. InP) and a catalytic material (e.g. Au) may be used to create a hot, dense vapor which condenses into liquid nanoclusters through collision with a buffer gas. Growth of the nanowire begins when the liquid nanoclusters become supersaturated with the desired phase and continues as long as the reactant is available.

Gold (Au) is generally used as catalyst for growing a wide range of elongated
10 nanoscale semiconductors. However, the catalyst is not limited to Au only. A wide range of materials such as Ag, Cu, Zn, Cd, Fe, Ni, Co, etc. can also be used as the catalyst. Generally, any metal that can form an alloy with the desired semiconductor material, but does not form more stable compound than with the elements of the desired semiconductor can be used as the catalyst. The buffer gas can be Ar, N₂, and/or other
15 inert gases. Sometimes, a mixture of H₂ and buffer gas is used to avoid undesired oxidation by residual oxygen. The reactive gas can also be introduced when desired (e.g. ammonia for GaN). Laser ablation may thus be used to generate liquid nanoclusters that subsequently define the size and direct the growth direction of the crystalline wires. The diameters of the resulting wires may be determined by the size of the catalyst cluster,
20 which in turn can be varied by controlling the growth conditions (e.g. background pressure, temperature, flow rate, etc.). For example, lower pressure generally produces wires with smaller diameters. Further diameter control can be done by using uniform diameter catalytic clusters.

With same basic principle as LCG, if uniform diameter nanoclusters (less than
25 about 10% to about 20% variation, depending on factors such as how uniform the nanoclusters are) are used as the catalytic cluster, wires with uniform size (diameter) distribution can be produced, where the diameter of the wires may be determined by the size of the catalytic clusters.

Surprisingly, growth of the wire is not necessarily terminated when the wire
30 passes out of the hot reaction zone and/or when the temperature is turned down. To the contrary, although growth rates are strongly affected by temperature, illustrating that decomposition kinetics prevails over gas phase mass-transport, the growth rate can be further increased at higher temperatures by accelerating the decomposition step, whereas

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side effects such as uncatalyzed deposition at the sidewall may determine the upper limit of temperature. Certain chemical vapor sources, such as Si_2H_6 , can be used to achieve this result. Such chemical vapor sources may be chosen by those of ordinary skill in the art by selecting chemical vapor sources having relatively low activation energies, for example, an activation energy for decomposition of a bond involving Si that is less than the Si-H bond in SiH_4 , which may result in a higher catalytic decomposition rate and thus facilitate extended growth of the wire. Accordingly, growth of the wire can be facilitated by increasing the decomposition kinetics without increasing temperature. As another non-limiting example, Ge_2H_6 may have a lower activation energy than GeH_4 , and Ge_2H_6 can be used to synthesize long germanium wires.

With LCG and similar techniques, the wires can also be flexibly doped by introducing one or more dopants into the composite target, e.g. Ge for n-type doping of InP, B_2H_6 for p-type doping of Si, etc. The doping concentration can be controlled by controlling the relative amount of doping element, typically 0%, 10%, or 20%, introduced in the composite target.

Laser ablation may be used to generate the catalytic clusters and vapor phase reactant for growth of wires and other related nanoscale structures, but fabrication is not limited to laser ablation. Many other ways can be used to generate vapor phase and catalytic clusters for wire growth (e.g. thermal evaporation), as is known by those of ordinary skill in the art.

Another technique that may be used to grow wires such as semiconductor nanowires is chemical vapor deposition (CVD). CVD utilizes the same basic principles as LCG, except that in CVD method, the reactant molecules (e.g., silane and/or Si_2H_6 and the dopant) are from vapor phase molecules (as opposed to a vapor source from, e.g., laser vaporization). The wires can be doped by introducing doping elements into the vapor phase reactant (e.g. diborane and phosphane for p-type and n-type doping, respectively). The doping concentration can be controlled, for instance, by controlling the relative amount of the doping element introduced in the composite target. By controlling the growth conditions (e.g. temperature, pressure, etc.), wires with same doping concentration can be reproduced. Doping concentrations can be varied over a large range by simply varying the ratio of gas reactant (e.g. about 1 ppm to about 10%), and proper vapor phase reactant concentrations to achieve a certain level of doping can be found using routine experimentation. In some embodiments, due to the use of Si_2H_6 ,

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lower growth temperatures may be used, as compared to deposition using silane. Such growth lower temperatures may be used since Si_2H_6 is more reactive than SiH_4 . For example, Si nanowires may be synthesized at temperature of between about 300°C and about 500°C, or between about 370 °C and about 410 °C (e.g., at about 400 °C) using Si_2H_6 , according to one embodiment of the invention.

Using one or more of the above techniques, wires such as semiconductor nanowires, or portions thereof, can be grown. Such wires may include, in some instances, various combinations of materials, including semiconductors and/or dopants, including the dopants previously described. Additional, non-limiting examples of LCG and other techniques are described in U.S. Patent Application Serial No. 09/935,776, filed August 22, 2001, entitled "Doped Elongated Semiconductors, Growing Such Semiconductors, Devices Including Such Semiconductors, and Fabricating Such Devices," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2002/0130311 on September 19, 2002, incorporated herein by reference.

One aspect of the invention is directed to articles and devices involving the wires of the invention. For example, the wires of the invention can be used in any electronic device. Examples of such devices include, but are not limited to, transistors such as field effect transistors (FETs) and/or bipolar junction transistors (BJTs), as well as diodes such as tunnel diodes, complementary inverters, light emitting devices, light sensing devices, sensors, memories, photovoltaic cells, gates, inverters, AND, NAND, OR, and NOR gates, latches, flip-flops, registers, switches, clock circuitry, static or dynamic memory devices and arrays, state machines, gate arrays, and any other dynamic or sequential logic or other digital devices including programmable circuits. Also included are analog devices and circuitry, including but not limited to, amplifiers, switches and other analog circuitry using active transistor devices, as well as mixed signal devices and signal processing circuitry.

In one set of embodiments, a wire of the invention is used as a component of a relatively large number of electronic elements, for example, transistors. For instance, at least about 25, 50, 100, 150, 200, 500, 750, 1000, or 2000 transistors may be fabricated along the length of one common wire of the invention. An example schematic diagram is shown in Fig. 3C, and non-limiting examples of such wires can be seen in Figs. 3D.

In one aspect, the present invention provides a sensing element comprising a wire such as a semiconductor nanowire able to interact with one or more analytes. For

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example, the nanoscale wire may be used to determine an analyte as part of an assay for determining or diagnosing a medical condition (e.g., by determining a suitable marker, for example, a hormone, an enzyme, a peptide, a virus, etc., and diagnosing the medical condition based on the determination of the marker), for determining drugs (e.g., as part of a drug assay or a drug screen, for instance, to identify a drug able to treat a medical condition such as cancer or aging), for determining toxins or other environmental agents (e.g., by determining binding of the toxin to a receptor), or the like.

The nanoscale wire may have associated therewith a reaction entity able to interact with an analyte of interest. Nanoscale sensing elements of the invention may be used, for example, to determine pH or metal ions, viruses, proteins or enzymes, nucleic acids (e.g. DNA, RNA, PNA, etc.), drugs, sugars, carbohydrates, small molecules (e.g., having molecular weights of less than about 2000 Da, less than about 1500 Da, or less than about 1000 Da), or other analytes of interest. In certain embodiments, single entities may be determined, for example, a single virus, a single protein, a single enzyme, a single nucleic acid molecule, a single drug molecule, a single carbohydrate molecule, etc. In some cases, the sensing element includes a detector constructed and arranged to determine a change in a property of a wire, for example, a change in light emission, a change in stress or shape, or a change in an electrical property of the nanoscale wire, such as voltage, current, conductivity, resistivity, inductance, impedance, electrical change, an electromagnetic change, etc. In one set of embodiments, at least a portion of the wire is addressable by a sample (e.g., a gas or liquid sample) containing, or at least suspected of containing, the analyte. The term "addressable," e.g., by a fluid, is defined as the ability of the fluid to be positioned relative to the wire so that the analytes suspected of being in the fluid are able to interact with the wire. The fluid may be proximate to or in contact with the wire. In some embodiments, the fluid may be directed to the wire through the use of a microfluidic channel, as further described below.

As used herein, the term "reaction entity" refers to any entity that can interact with an analyte in such a manner as to cause a detectable change in a property of a wire of the invention. The reaction entity may comprise a binding partner to which the analyte binds. The reaction entity, when a binding partner, can comprise a specific binding partner of the analyte. In some cases, the reaction entity can form a coating on the nanoscale wire. Non-limiting examples of reaction entities include a nucleic acid

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(e.g., DNA or RNA), an antibody, a sugar or a carbohydrate, a protein or an enzyme, etc., e.g., as discussed herein.

In one set of embodiments, a reaction entity associated with the wire is able to interact with an analyte. The reaction entity, as "associated" with or "immobilized" relative to the wire, may be positioned in relation to the wire (e.g., in close proximity or in contact) such that the analyte can be determined by determining a change in a characteristic or property of the wire. Interaction of the analyte with the reaction entity may cause a detectable change or modulation in a property of the wire, for example, through electrical coupling with the reaction entity. The term "electrically coupled" or "electrocoupling," when used with reference to a wire and an analyte, or other moiety such as a reaction entity, refers to an association between any of the analyte, other moiety, and the wire such that electrons can move from one to the other, or in which a change in an electrical characteristic of one can be determined by the other. This can include electron flow between these entities, or a change in a state of charge, oxidation, or the like, that can be determined by the wire. As examples, electrical coupling or immobilization can include direct covalent linkage between the analyte or other moiety and the nanoscale wire, indirect covalent coupling (for instance, via a linker, and/or a plurality of linkers, e.g., serially), direct or indirect ionic bonding between the analyte (or other moiety) and the wire, direct or indirect bonding of both the analyte and the wire to a particle (i.e., the particle acts as a linker between the analyte and the wire), direct or indirect bonding of both the analyte and the wire to a common surface (i.e., the surface acts as a linker), or other types of bonding or interactions (e.g. hydrophobic interactions or hydrogen bonding). In some cases, no actual covalent bonding is required; for example, the analyte or other moiety may simply be contacted with the nanoscale wire surface. There also need not necessarily be any contact between the wire and the analyte or other moiety where the nanoscale wire is sufficiently close to the analyte to permit electron tunneling between the analyte and the wire.

Thus, the reaction entity may be positioned relative to the wire to cause a detectable change in the wire. In some cases, the reaction entity may be positioned within about 100 nm of the wire, within about 75 nm of the wire, within about 50 nm of the wire, within about 20 nm of the wire, within about 15 nm of the wire, or within about 10 nm of the wire. The actual proximity can be determined by those of ordinary skill in the art. In some cases, the reaction entity is positioned less than about 5 nm from the

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wire. In other cases, the reaction entity is positioned within about 4 nm, within about 3 nm, within about 2 nm, or within about 1 nm of the wire.

In some embodiments, the reaction entity is fastened to or directly bonded (e.g., covalently) to the wire, e.g., as further described herein. However, in other
5 embodiments, the reaction entity is not directly bonded to the nanoscale wire, but is otherwise immobilized relative to the nanoscale wire, i.e., the reaction entity is indirectly immobilized relative to the nanoscale wire. For instance, the reaction entity may be attached to the nanoscale wire through a linker, i.e., a species (or plurality of species) to which the reaction entity and the nanoscale wire are each immobilized relative thereto,
10 e.g., covalently or non-covalently bound to. Non-limiting examples of systems and methods that can be readily adapted to be used to link one or more reaction entities to a wire of the present invention are discussed in U.S. Patent Application Serial No. 11/501,466, filed August 9, 2006, entitled "Nanoscale Sensors," by Lieber, *et al.*, incorporated herein by reference.

15 Also provided, according to another set of embodiments, is a sensing element comprising a wire of the present invention and a detector constructed and arranged to determine a property and/or a change in a property of the wire. In some cases, alteration of a property of the wire may be indicative of an interaction between a reaction entity and an analyte (e.g., association or dissociation of the reaction entity and the analyte).
20 Where a detector is present, any detector capable of determining a property associated with the wire can be used. The property can be electronic, electromagnetic, optical, mechanical, or the like. Examples of electrical or magnetic properties that can be determined include, but are not limited to, voltage, current, conductivity, resistance, impedance, inductance, charge, etc. Non-limiting examples of optical properties
25 associated with the wire include its emission intensity and/or emission wavelength, e.g. where the wire is emissive. In some cases, the detector will include a power source and a metering device, for example a voltmeter or an ammeter.

In one embodiment, a conductance (or a change in conductance) less than about 1 nS in a wire sensor of the invention can be detected. In another embodiment, a
30 conductance in the range of thousandths of a nS can be detected. In other embodiments, conductances of less than about 10 microsiemens, less than about 1 microsiemen, less than about 100 nS, or less than about 10 nS can be detected. The concentration of a species, or analyte, may be detected from femtomolar concentrations, to nanomolar,

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micromolar, millimolar, and to molar concentrations and above. By using wires with known detectors, sensitivity can be extended to a single molecules in some cases.

As a non-limiting example, a charged analyte may be determined by determining a change in an electrical property of the wire, for example, conductivity. Immobilizing a charged analyte relative to the wire may cause a change in the conductivity of the wire, and in some cases, the distance between the charged analyte and the wire may determine the magnitude of the change in conductivity of the wire. Uncharged analytes can be similarly determined, for instance, by causing the analyte to become charged, e.g., by altering environmental conditions such as pH (by raising or lowering pH), temperature, reactants, or the like, by reacting the analyte with a charged moiety, or the like.

The analyte to be determined by the sensor may be present within a sample. The term "sample" refers to any cell, lysate, tissue, or fluid from a biological source (a "biological sample"), or any other medium, biological or non-biological, that can be evaluated in accordance with the invention. The sample may be, for instance, a liquid (e.g., a solution or a suspension) or a gas. A sample includes, but is not limited to, a biological sample drawn from an organism (e.g. a human, a non-human mammal, an invertebrate, a plant, a fungus, an algae, a bacteria, a virus, etc.), a sample drawn from food designed for human consumption, a sample including food designed for animal consumption such as livestock feed, milk, an organ donation sample, a sample of blood destined for a blood supply, a sample from a water supply, a soil sample, or the like.

In some cases, the sample may be a sample suspected of containing an analyte. A "sample suspected of containing" a particular component means a sample with respect to which the content of the component is unknown. For example, a fluid sample from a human suspected of having a disease, but not known to have the disease, defines a sample suspected of containing the disease. "Sample" in this context includes naturally-occurring samples, such as physiological samples from humans or other animals, samples from food, livestock feed, water, soil, etc. Typical samples include tissue biopsies, cells, cell lysates, whole blood, serum or other blood fractions, urine, ocular fluid, saliva, fluid or other samples from tonsils, lymph nodes, needle biopsies, etc.

A variety of sample sizes, for exposure of a sample to a sensor of the invention, can be used in various embodiments of the invention. As examples, the sample size used in sensors may be less than or equal to about 10 microliters, less than or equal to about 1 microliter, or less than or equal to about 0.1 microliter. The sample size may be as small

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as about 10 nanoliters, 1 nanoliter, or less, in certain instances. The sensor also allows for unique accessibility to biological species and may be used for *in vivo* and/or *in vitro* applications.

The invention, in some embodiments, involves a sensing element comprising a sample exposure region and a wire able to detect the presence or absence of an analyte, and/or the concentration of the analyte. The "sample exposure region" may be any region in close proximity to the wire where a sample in the sample exposure region addresses at least a portion of the wire. Examples of sample exposure regions include, but are not limited to, a well, a channel, a microfluidic channel, or a gel. In certain
10 embodiments, the sample exposure region is able to hold a sample proximate the wire, and/or may direct a sample toward the wire for determination of an analyte in the sample. The wire may be positioned adjacent or within the sample exposure region. Alternatively, the wire may be a probe that is inserted into a fluid or fluid flow path. The wire probe may also comprise, in some instances, a microneedle that supports and/or is
15 integral with the wire, and the sample exposure region may be addressable by the microneedle. In this arrangement, a device that is constructed and arranged for insertion of a microneedle probe into a sample can include a region surrounding or otherwise in contact with the microneedle that defines the sample exposure region, and a sample in the sample exposure region is addressable by the wire, and vice versa. Fluid flow
20 channels can be created at a size and scale advantageous for use in the invention (microchannels) using a variety of techniques such as those described in International Patent Application Serial No. PCT/US97/04005, entitled "Method of Forming Articles and Patterning Surfaces via Capillary Micromolding," filed March 14, 1997, published as Publication No. WO 97/33737 on September 18, 1997, incorporated herein by
25 reference.

As a non-limiting example, a sample, such as a fluid suspected of containing an analyte that is to be determined, may be presented to a sample exposure region of a sensing element comprising a wire. An analyte present in the fluid that is able to bind to the wire and/or a reaction entity immobilized relative to the wire may cause a change in a
30 property of the wire that is determinable upon binding, e.g. using conventional electronics. If the analyte is not present in the fluid, the relevant property of the wire will remain unchanged, and the detector will measure no significant change. Thus, according to this particular example, the presence or absence of an analyte can be determined by

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monitoring changes, or lack thereof, in the property of the wire. In some cases, if the detector measures a change, the magnitude of the change may be a function of the concentration of the analyte, and/or a function of some other relevant property of the analyte (e.g., charge or size, etc.). Thus, by determining the change in the property of the wire, the concentration or other property of the analyte in the sample may be determined.

In some embodiments, one or more wires may be positioned in a channel or in a microfluidic channel, which may define the sample exposure region in some cases. As used herein, a "channel" is a conduit that is able to transport one or more fluids specifically from one location to another. Materials may flow through the channels, continuously, randomly, intermittently, etc. The channel may be a closed channel, or a channel that is open, for example, open to the external environment. The channel can include characteristics that facilitate control over fluid transport, e.g., structural characteristics, physical/chemical characteristics (e.g., hydrophobicity vs. hydrophilicity) and/or other characteristics that can exert a force (e.g., a containing force) on a fluid when within the channel. The fluid within the channel may partially or completely fill the channel. In some cases the fluid may be held or confined within the channel or a portion of the channel in some fashion, for example, using surface tension (i.e., such that the fluid is held within the channel within a meniscus, such as a concave or convex meniscus). The channel may have any suitable cross-sectional shape that allows for fluid transport, for example, a square channel, a circular channel, a rounded channel, a rectangular channel (e.g., having any aspect ratio), a triangular channel, an irregular channel, etc. The channel may be of any size. For example, the channel may have a largest dimension perpendicular to a direction of fluid flow within the channel of less than about 1000 micrometers in some cases (i.e., a microfluidic channel), less than about 500 micrometers in other cases, less than about 400 micrometers in other cases, less than about 300 micrometers in other cases, less than about 200 micrometers in still other cases, less than about 100 micrometers in still other cases, or less than about 50 or 25 micrometers in still other cases. In some embodiments, the dimensions of the channel may be chosen such that fluid is able to freely flow through the channel. The dimensions of the channel may also be chosen in certain cases, for example, to allow a certain volumetric or linear flowrate of fluid within the channel. Of course, the number of channels, the shape or geometry of the channels, and the placement of channels can be determined by those of ordinary skill in the art.

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One or more different wires may cross the same microfluidic channel (e.g., at different positions) to detect the same or different analytes, to measure a flowrate of an analyte(s), etc. In another embodiment, one or more wires may be positioned in a microfluidic channel to form one of a plurality of analytic elements, for instance, in a microneedle probe, a dip and read probe, etc. The analytic elements probe may be implantable and capable of detecting several analytes simultaneously in real time, according to certain embodiments. In another embodiment, one or more wires may be positioned in a microfluidic channel to form an analytic element in a microarray for a cassette or a lab-on-a-chip device. Those of ordinary skill in the art would know of examples of cassette or lab-on-a-chip devices that are suitable for high-throughout chemical analysis and screening, combinational drug discovery, etc. The ability to include multiple wires in one sensor also allows, in some cases, for the simultaneous detection of different analytes suspected of being present in a single sample, i.e., the sensor allows "multiplexed" detection of different analytes. For example, a sensor may include a plurality of wires that each detect different pH levels, proteins, enzymes, toxins, small molecules, and/or nucleic acids, etc.

In some cases, the sensing element may comprise a plurality of wires able to determine (i.e., detect the presence, absence, and/or amount or concentration) one or more analytes within a sample, for example, from a liquid or solution, blood serum, etc., as previously described. Various wires within the sensing element may contain different reaction entities, and/or the same reaction entities at different concentrations, thereby varying the sensitivity of the wires to the analytes, as needed. In some cases, individual nanoscale wires may be selected based on their ability to interact with specific analytes, thereby allowing the detection of a variety of analytes. The plurality of nanoscale wires may be randomly oriented or parallel to one another, according to another set of embodiments. The plurality of nanoscale wires may also be oriented in an array on a substrate, in specific instances. A sensing element of the present invention can collect real time data and/or near-real time data, in some embodiments. The data may be used, for example, to monitor the reaction rate of a specific chemical or biological reaction. Physiological conditions or drug concentrations present *in vivo* may also produce a real time (or near-real time) signal that may be used to control a drug delivery system, in another embodiment of the invention.

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In addition, electrical determination of one or more properties of the wire may allow for the determination of one or more analytes as a function of time. For example, the conductance of a wire may be determined as a function of time, which may give additional information regarding the analyte. In some cases, a wire of the invention may be exposed to a series of samples, and the properties of the wire, as determined as a function of time, may be related to the concentration of analyte within each of the samples. This feature may also, in some cases, be combined with the use of multiple wires to detect different analytes. Thus, in some embodiments, a sensing element of the invention may be used to detect multiple analytes in one or more samples.

In some cases, the wires, or at least a portion of the wires, may be individually addressable, i.e., the status of the wire may be determined without determining the status of nearby wires. Thus, for example, a wire within a sensing element, or a number of wires within the sensing element, may be in electrical communication with an electrode that is able to address the wire(s), and such a wire may be addressed using the electrode without addressing other wires not in electrical communication with the electrode. For example, a first reaction entity immobilized relative to a first wire may bind an analyte, and such a binding event may be detectable independently of the detection of a binding event involving a second reaction entity immobilized relative to a second wire. The electrodes may be in electronic communication with one or more electrical contacts.

As an example, the present invention includes, in some embodiments, an integrated system comprising a wire detector, a reader, and a computer controlled response system. In this example, the wire detects a change in the equilibrium or concentration of an analyte in the sample, feeding a signal to the computer controlled response system, causing it to withhold or release a chemical or drug. That is, the knowledge of those of ordinary skill in the art, coupled with the disclosure herein of wires as sensors, real-time measurement devices, integrated systems, or the like. Such systems can be made capable of monitoring one, or a plurality of, physiological characteristics individually or simultaneously. Such physiological characteristics can include, for example, oxygen concentration, carbon dioxide concentration, glucose level, concentration of a particular drug or molecule, concentration of a particular drug by-product, concentration of an enzyme or protein, concentration of a toxin, or the like. Integrated physiological devices can be constructed to carry out a function depending upon a condition sensed by a sensor of the invention.

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The present invention finds use in a wide range of applications. For instance, in one set of embodiments, any of the techniques described herein may be used in the determination of proteins, enzymes, toxins, viruses, small molecules, or the like, e.g., as in an assay, for example, to detect or diagnose cancer or other medical conditions, toxins
5 or other environmental agents, viruses, or the like. A property of an analyte may be determined by allowing the analyte to interact with a wire and/or a reaction entity, and the interaction may be analyzed or determined in some fashion, e.g., quantified. In some cases, the degree or amount of interaction (e.g., a binding constant) may be determined, for example, by measuring a property of the wire (e.g., an electronic property, such as the
10 conductance) after exposing the wire and/or the reaction entity to the analyte.

The following documents are incorporated herein by reference in their entirety for all purposes, and include additional description of teachings usable with the present invention: U.S. Patent Application Serial No. 09/935,776, filed August 22, 2001, entitled "Doped Elongated Semiconductors, Growing Such Semiconductors, Devices
15 Including Such Semiconductors, and Fabricating Such Devices," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2002/0130311 on September 19, 2002; U.S. Patent Application Serial No. 10/033,369, filed October 24, 2001, entitled "Nanoscopic Wire-Based Devices and Arrays," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2002/0130353 on September 19, 2002, now U.S.
20 Patent No. 6,781,166, issued August 24, 2004; U.S. Patent Application Serial No. 10/020,004, filed December 11, 2001, entitled "Nanosensors," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2002/0117659 on August 29, 2002; U.S. Patent Application Serial No. 10/152,490, filed May 20, 2002, entitled "Nanoscale Wires and Related Devices," by Lieber, *et al.*; U.S. Patent Application Serial No.
25 10/196,337, filed July 16, 2002, entitled "Nanoscale Wires and Related Devices," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2003/0089899 on May 15, 2003; U.S. Patent Application Serial No. 10/720,020, filed November 21, 2003, entitled "Nanoscale Wires and Related Devices," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2003/0089899 on May 15, 2003; U.S. Patent
30 Application Serial No. 10/812,653, filed March 29, 2004, entitled "Nanoscopic Wire-Based Devices and Arrays," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2004/0188721 on September 30, 2004; U.S. Patent Application Serial No. 10/973,665, filed October 26, 2004, entitled "Nanoscopic Wire-Based Devices and

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Arrays," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2005/0117441 on June 2, 2005; U.S. Patent Application Serial No. 10/995,075, filed November 22, 2004, entitled "Nanoscale Arrays and Related Devices," by Whang, *et al.*, published as U.S. Patent Application Publication No. 2005/0253137 on November 17, 2005; U.S. Patent Application Serial No. 11/058,443, filed February 14, 2005, entitled "Nanoscale Wires and Related Devices," by Lieber, *et al.*; International Patent Application No. PCT/US2005/004459, filed February 14, 2005, entitled "Nanostructures Containing Metal-Semiconductor Compounds," by Lieber, *et al.*, published as WO 2005/093831 on October 6, 2005; U.S. Patent Application Serial No. 11/137,784, filed May 25, 2005, entitled "Nanoscale Sensors," by Lieber, *et al.*; U.S. Provisional Patent Application Serial No. 60/707,136, filed August 9, 2005, entitled "Nanoscale Sensors," by Lieber, *et al.*; U.S. Provisional Patent Application Serial No. 60/790,322, filed April 7, 2006, entitled "Nanoscale Wire Methods and Devices," by Lieber, *et al.*; U.S. Provisional Patent Application Serial No. 60/812,884, filed June 12, 2006, entitled "Nanosensors and Related Technologies," by Lieber, *et al.*; and; U.S. Patent Application Serial No. 11/501,466, filed August 9, 2006, entitled "Nanoscale Sensors," by Lieber, *et al.* Also incorporated herein by reference is U.S. Provisional Patent Application Serial No. 60/860,460, filed November 21, 2006, entitled "Millimeter-Long Nanowires," by Park, *et al.*

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The following examples are intended to illustrate certain embodiments of the present invention, but do not exemplify the full scope of the invention.

EXAMPLE 1

This example illustrates the synthesis of long nanowires. The technique shown in this example shows that the overall growth rate of a nanowire can be promoted by accelerating the rate-limiting step in a VLS (vapor-liquid-solid) process. VLS is a continuous process including catalytic adsorption of gaseous reactants at the surface of a liquid nanoparticle, diffusion through the liquid, and precipitation at the liquid-solid interface between the liquid and the growing nanowire, thereby elongating the nanowire. The basic crystallization, however, is relatively similar to traditional bulk solidification process from liquid solutions or melts.

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As shown in this example, an important factor that controls nanowire growth is supersaturation within the liquid catalyst, although the supersaturation can be controlled

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by the continuous adsorption of reactants through the catalyst surface, since the nanowires are grown at a constant temperature. Accordingly, as shown here, the overall growth rate in the VLS process may be determined by gas-phase kinetics, i.e., the interplay between mass transport and decomposition of precursor gas to/at the catalyzing liquid surface. Previously, it has been shown that single-crystal Si nanowires could be synthesized by chemical vapor deposition (CVD) with growth rates reaching up to 1 to 2 micrometers/min by using SiH_4 as the gas precursor. See U.S. Patent Application Serial No. 09/935,776, filed August 22, 2001, entitled "Doped Elongated Semiconductors, Growing Such Semiconductors, Devices Including Such Semiconductors, and Fabricating Such Devices," by Lieber, *et al.*, published as U.S. Patent Application Publication No. 2002/0130311 on September 19, 2002, incorporated herein by reference.

Experiments around this growth regime show that the growth rates were strongly affected by temperature, illustrating that decomposition kinetics prevails over gas phase mass transport. Therefore, the growth rate could be further increased at higher temperatures by accelerating the decomposition step, whereas side effects such as uncatalyzed deposition at the nanowire sidewall determine the upper limit of temperature. Thus, to explore the new nanowire growth regime by boosting decomposition kinetics without increasing temperature, Si_2H_6 was introduced as an alternative chemical vapor source. Si_2H_6 has a much higher catalytic decomposition rate, which is believed to be due to the lower activation energy for the decomposition of Si-Si bond than that for the Si-H bond in SiH_4 .

Si nanowires were synthesized by CVD using well-dispersed gold nanoclusters as the catalyst and Si_2H_6 as a reactant source. The Si nanowires were synthesized at 400 °C using 10 nm, 20 nm, or 30 nm gold nanoclusters as catalysts, H_2 as a carrier gas (10 cm^3 at standard temperature and pressure, STM min^{-1}), and Si_2H_6 (3 STM min^{-1}) as a reactant source at 10 torr. The use of Si_2H_6 may provide advantages such as low growth temperature around 380 °C to 400 °C (which is roughly 50 °C lower than that for SiH_4), and/or elongation of nanowire lengths to millimeter-scale, as discussed in these examples. Examples of such Si nanowires are shown in Fig. 1A, which is a scanning electron microscopy (SEM) image of the Si nanowires after being synthesized using Si_2H_6 at 400 °C for 30 min. The scale bar is 20 micrometers.

Quantitative analysis showed that the average length of Si nanowires grown for 1 h is about 1.8 mm, and that the longest ones reached 3.5 mm, with substantially uniform

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diameters determined by the starting gold nanocluster size. Since these long wires were easily bent or entangled together, and often broken into small pieces during solution-based transfer and assembly, a soft-dry-transfer method was developed to transfer the nanowires directly from the growth substrate onto a device substrate. Briefly, the growth wafers containing the Si nanowires were first fixed and inclined with a 30° to 60° slope. Oxidized silicon wafers were put opposite the growth wafers. Then, the oxidized silicon wafers were allowed to glide down the slope on the growth wafers by gravity. During the glide of the wafers, the frictional force facilitated transfer of at least some of the nanowires from growth wafers to the oxidized silicon wafers, and alignment along the transferring direction. The gliding speed could also be easily controlled by adjusting the gliding angle.

During the transfer, the frictional force between substrates and the nanowires caused the nanowires to spread out and become aligned along the transferring direction. A series of 20 SEM images of a well isolated, 2.3-mm-long Si nanowire are shown in Fig. 1B, which shows a nanowire after it was transferred onto a SiO₂/Si substrate. The scale bar is 200 micrometers. The insets in Fig. 1B show SEM images of the starting and end segments of this nanowire. The diameters along the nanowire are substantially uniform, with starting and end points of about 32 nm and about 33 nm, respectively. This substantially uniform diameter distribution may represent the limited over-coating during the synthesis, which may indicate that Si₂H₆ decomposition is highly selective to the liquid catalyst surface, rather than at the Si surface during low temperature growth. Fig. 1C is a dark-field optical image of the same nanowire. The scale bar is 500 micrometers. It should be noted that the nanowire is more clearly shown in dark-field optical image, which originates from light scattering at the nanowire surface.

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EXAMPLE 2

To confirm that fast nanowire growth originated from the fast decomposition of Si₂H₆ at the liquid catalyst surface, this example compares the growth rates for Si₂H₆ with that for SiH₄ by fixing all of the conditions except those for the growth temperature. Fig. 2A is a plot of nanowire length versus growth time for SiH₄ at 400 °C, 450 °C, and for Si₂H₆ at 400 °C, respectively, corresponding to the growth rates of 0.24, 1.0, 31 micrometers/min.

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The average nanowire growth rate for Si₂H₆ at 400 °C was about 31 micrometers/min, which is about 130 times higher than that for SiH₄ at the same

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temperature, and about 31 times higher than for SiH_4 at the optimal growth temperature of 450 °C. Due to the lack of decomposition data at the liquid catalyst surface, decomposition coefficients in the gas phase were taken instead and compared with the corresponding growth rates. A simple calculation showed that the decomposition rate ratios for Si_2H_6 at 400 °C over SiH_4 at 400 °C and 450 °C were roughly 170 and 10, respectively. These values were similar to the ratios of actual growth rates, and this result may represent the role of gas-phase decomposition kinetics in determining the nanowire growth rate.

Additionally, the structural characteristics of the Si nanowires synthesized in the ultra-fast growth regime were investigated by high-resolution transmission electron microscopy (HR-TEM). Fig. 2B shows an HR-TEM image of an ultralong Si nanowire with a diameter of about 18 nm. The scale bar is 5 nm. As shown, highly ordered lattice images were observed, indicating that these Si nanowires were well crystallized, even though they were formed very rapidly. In addition, two-dimensional (2D) Fourier transform data in Fig. 2B shows the [111] zone axis and a $\langle 110 \rangle$ growth direction (inset). The six inner peaks are forbidden $1/3 \{422\}$ reflections that arise due to the finite thickness of the nanowire. Significantly, a preliminary survey from more than 30 wires showed that all of the wires were substantially oriented along the $\langle 110 \rangle$ direction. This result is surprising considering that the general Si nanowire growth behavior has a preference for growth along the $\langle 110 \rangle$ direction in smaller diameter Si nanowires, and along the $\langle 111 \rangle$ direction in larger Si nanowires, with a crossover diameter between these regimes of about 20 nm.

To determine whether the crossover of growth direction for the Si nanowires discussed above also exists in the ultra-fast growth regime, the nanowire diameters were controlled from 40 nm to 130 nm by utilizing different sizes of gold catalysts, and the growth orientations were carefully investigated based on the nanowire diameters. It was observed that most of the nanowires grew along the $\langle 110 \rangle$ direction and no evidence of transition to other directions was ever observed (Fig. 2C). This figure is an HR-TEM image of an ultralong Si nanowire with a diameter of about 80 nm. The scale bar is 5 nm. The upper inset is a 2D Fourier transform of the lattice image. The six inner peaks are forbidden $1/3 \{422\}$ reflections. The lower inset shows a low magnification TEM image.

EXAMPLE 3

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In this example, diborane (B_2H_6) was introduced as a p-type doping source during synthesis, and various fundamental electrical characteristics of Si nanowires were investigated by preparing field effect transistor (FET) arrays with a back gate geometry (Figs. 3A-3D). Fig. 3A shows a schematic of multiple FETs fabricated on a p-Si nanowire. Briefly, millimeter-long p-type Si nanowires were synthesized using 100 ppm B_2H_6 as the doping source with a $Si_2H_6:B_2H_6$ ratio of 10^5 to $2 \times 10^5:1$ ($Si:B = 10^5$ to $2 \times 10^5:1$). The nanowires were then transferred to degenerately doped (resistivity < 0.005 Ohm cm) silicon (100) substrates coated with 50-nm-thick SiO_2 (Silicon Valley Microelectronics, Inc., San Jose, CA). Multiple electrodes to the long wires were defined by electron-beam (e-beam) lithography (JEOL JSM-7000F incorporated with Naby's Nanometer Pattern Generation System V9.0), followed by evaporation of 70-nm-thick Ni contacts. Rapid thermal annealing was carried out at 280 °C for 1 min in the formation gas (10% H_2 in He).

Fig. 3B is a low magnification SEM image of multiple FETs defined by e-beam lithography. The scale bar is 1 mm. Fig. 3C is an enlarged SEM image of multiple FETs corresponding to the square in Fig. 3B. The 2-micrometer-thick strip patterns were separated by 2 micrometers. The insets show high magnification SEM images corresponding to these squares, showing that the wires had substantially uniform diameters. Small increases in diameter toward the right side might be due to uncatalyzed deposition at wire surface by B_2H_6 -assisted Si_2H_6 decomposition. Fig. 3D is a dark-field optical image of the same devices, showing the millimeter-scale wire below the electrode arrays. The scale bar is 100 micrometers.

Source-drain current (I_D) versus source-drain voltage (V_D) curves recorded at different gate voltages (V_G) for a typical device having multiple FETs appeared to be linear at the low voltage bias (Fig. 3E), representing the low resistance ohmic contacts between the Si and Ni metal layers. The curves in this figure illustrate various V_G values of -10 V, -5 V, 0 V, 5 V, and 10 V, respectively. In addition, as V_D increased positively (negatively), I_D decreased (increased) for p-type Si nanowire FETs. Typical I_D - V_G curves of randomly chosen FETs (Fig. 3F) also showed that the devices operated in a depletion (normally on) mode with a threshold voltage (V_{th}) of 5 V to 7 V. From a logarithmic plot of I_D - V_G , the current on/off ratio and the subthreshold slope were estimated to be about 10^4 to 10^6 and 200 mV/dec (decade) to 500 mV/dec, respectively. In addition, the peak transconductance ($G_M = dI_D/dV_G$) was estimated to be about 160 nS

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to 270 nS, with a maximum value of about 360 nS, corresponding to a calculated hole mobility of about $80 \text{ cm}^2/\text{V}\cdot\text{s}$. This mobility value is comparable to previous single p-Si nanowire FETs.

To assess the electrical properties along the millimeter-length wires, important transistor characteristics of on-state I_D , G_M , and V_{th} were investigated systematically and are depicted in Figs. 3G-3I, respectively. More than 90% of devices prepared here behaved as proper FETs and exhibited substantially uniform electrical properties along the wires, indicating homogeneous electrical doping during synthesis. It should be noted that the defects in these devices (appearing in below 10% of the devices) might have resulted from fabrication failures such as electrical shorts, disconnections, and poor contacts, which can be further reduced, without an undue amount of experimentation, using more careful designing and fabrication processes and routine optimization. Fig. 3G shows position vs. I_D at $V_D = 1 \text{ V}$ and $V_G = -10 \text{ V}$ measured from the single-nanowire multiple FETs in Figs. 3C and 3D. The I_D measured along the single nanowire exhibited a mean of about 1.77 microamperes and a standard deviation of about 0.326 microamperes. Fig. 3H shows position vs. G_M at $V_D = 1 \text{ V}$, with a mean of about 213 nS and a standard deviation of about 60.6 nS. Fig. 3I shows position vs. V_{th} , with a mean of about -5.98 V and a standard deviation of about 1.10 V.

EXAMPLE 4

In this example, multiple FETs were used as biological sensor arrays by functionalizing the Si nanowire surfaces with monoclonal antibodies (mAbs), and were used to illustrate multiplexed electrical detection of cancer markers.

Fig. 4A is an optical image of a multiple sensor array used in some of the following experiments. Both the widths of the metal electrodes and the nanowire channels were 2 micrometers. The scale bar is 100 micrometers. Another image can be seen in Fig. 6. Fig. 4B shows conductance versus time data recorded simultaneously from a sampling of Si nanowire devices functionalized with prostate specific antigen (PSA)-Ab1 receptors after introduction of target protein solutions. The data were recorded with alternative delivery of target solutions (PSA or BSA) and pure buffers (1 micromolar phosphate containing 2 micromolar KCl, pH of 7.4). The vertical arrows corresponded to the delivery of (1) 20 pg/ml PSA, (2) 500 pg/ml PSA, (3) 10 ng/ml PSA, (4) 10 micrograms/ml BSA, and (5) 20 pg/ml PSA solutions, sequentially.

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All of the devices prepared here showed a well-defined conductance increase and subsequent restoration to baseline with the alternate delivery of PSA and pure buffer solutions. In addition, the conductance change increased with increasing PSA concentration, whereas no conductance change was shown with the delivery of 10 micrograms/ml bovine serum albumin (BSA) solution. The selective response to PSA solutions indicated that the conductance changes resulted from PSA binding to the Abl receptors linked on the Si nanowire surfaces, and represents the capability of the single nanowires prepared here as multiple biological sensors.

Simultaneous monitoring of the signals from multiple sensors may provide the opportunity to distinguish between low-level real signals and noises more distinctly, since all of the devices can respond simultaneously to the arrival of a target protein, whereas noise signals, such as those from unspecific protein binding, are observed only from some devices independently (arrows in Fig. 4B). Although the present measurements were restricted to a small number of devices and also to a single protein category, there is believed to be no fundamental limit for the scale of this approach, and these millimeter-long Si nanowires thus can be used in more complex and multiplexed electrical detection by combining them with other semiconductor processing techniques and microfluidic technologies, for example, as discussed in U.S. Patent Application Serial No. 11/501,466, filed August 9, 2006, entitled "Nanoscale Sensors," by Lieber, *et al.*, incorporated herein by reference.

While several embodiments of the present invention have been described and illustrated herein, those of ordinary skill in the art will readily envision a variety of other means and/or structures for performing the functions and/or obtaining the results and/or one or more of the advantages described herein, and each of such variations and/or modifications is deemed to be within the scope of the present invention. More generally, those skilled in the art will readily appreciate that all parameters, dimensions, materials, and configurations described herein are meant to be exemplary and that the actual parameters, dimensions, materials, and/or configurations will depend upon the specific application or applications for which the teachings of the present invention is/are used. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. It is, therefore, to be understood that the foregoing embodiments are

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presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described and claimed. The present invention is directed to each individual feature, system, article, material, kit, and/or method described herein. In addition, any
5 combination of two or more such features, systems, articles, materials, kits, and/or methods, if such features, systems, articles, materials, kits, and/or methods are not mutually inconsistent, is included within the scope of the present invention.

All definitions, as defined and used herein, should be understood to control over dictionary definitions, definitions in documents incorporated by reference, and/or
10 ordinary meanings of the defined terms.

The indefinite articles "a" and "an," as used herein in the specification and in the claims, unless clearly indicated to the contrary, should be understood to mean "at least one."

The phrase "and/or," as used herein in the specification and in the claims, should
15 be understood to mean "either or both" of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Multiple elements listed with "and/or" should be construed in the same fashion, i.e., "one or more" of the elements so conjoined. Other elements may optionally be present other than the elements specifically identified by the "and/or" clause, whether related or
20 unrelated to those elements specifically identified. Thus, as a non-limiting example, a reference to "A and/or B", when used in conjunction with open-ended language such as "comprising" can refer, in one embodiment, to A only (optionally including elements other than B); in another embodiment, to B only (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other
25 elements); etc.

As used herein in the specification and in the claims, "or" should be understood to have the same meaning as "and/or" as defined above. For example, when separating items in a list, "or" or "and/or" shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and,
30 optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as "only one of" or "exactly one of," or, when used in the claims, "consisting of," will refer to the inclusion of exactly one element of a number or list of elements. In general, the term "or" as used herein shall only be interpreted as indicating exclusive alternatives

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(i.e. "one or the other but not both") when preceded by terms of exclusivity, such as "either," "one of," "only one of," or "exactly one of." "Consisting essentially of," when used in the claims, shall have its ordinary meaning as used in the field of patent law.

As used herein in the specification and in the claims, the phrase "at least one," in
5 reference to a list of one or more elements, should be understood to mean at least one
element selected from any one or more of the elements in the list of elements, but not
necessarily including at least one of each and every element specifically listed within the
list of elements and not excluding any combinations of elements in the list of elements.
This definition also allows that elements may optionally be present other than the
10 elements specifically identified within the list of elements to which the phrase "at least
one" refers, whether related or unrelated to those elements specifically identified. Thus,
as a non-limiting example, "at least one of A and B" (or, equivalently, "at least one of A
or B," or, equivalently "at least one of A and/or B") can refer, in one embodiment, to at
least one, optionally including more than one, A, with no B present (and optionally
15 including elements other than B); in another embodiment, to at least one, optionally
including more than one, B, with no A present (and optionally including elements other
than A); in yet another embodiment, to at least one, optionally including more than one,
A, and at least one, optionally including more than one, B (and optionally including other
elements); etc.

20 It should also be understood that, unless clearly indicated to the contrary, in any
methods claimed herein that include more than one step or act, the order of the steps or
acts of the method is not necessarily limited to the order in which the steps or acts of the
method are recited.

In the claims, as well as in the specification above, all transitional phrases such as
25 "comprising," "including," "carrying," "having," "containing," "involving," "holding,"
"composed of," and the like are to be understood to be open-ended, i.e., to mean
including but not limited to. Only the transitional phrases "consisting of" and
"consisting essentially of" shall be closed or semi-closed transitional phrases,
respectively, as set forth in the United States Patent Office Manual of Patent Examining
30 Procedures, Section 2111.03.

What is claimed is:

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CLAIMS

1. An article, comprising:
a semiconductor wire, including a portion having a length of at least about
5 0.3 mm and a thickness of no more than about 500 nm, and no more than about 1
grain boundary per micrometer.
2. The article of claim 1, wherein the wire has a length of at least about 0.5 mm.
- 10 3. The article of claim 2, wherein the wire has a length of at least about 1 mm.
4. The article of claim 1, wherein at least the portion of the semiconductor wire
comprises silicon.
- 15 5. The article of claim 1, wherein at least the portion of the semiconductor wire
consists essentially of silicon.
6. The article of claim 5, wherein the semiconductor wire consists essentially of
silicon.
- 20 7. The article of claim 5, wherein at least the portion of the semiconductor wire has
no more than about 1 grain boundary per 10 micrometers of semiconductor wire.
8. The article of claim 7, wherein at least the portion of the semiconductor wire has
25 no more than about 1 grain boundary per 100 micrometers of semiconductor
wire.
9. The article of claim 1, wherein at least the portion of the semiconductor wire is a
single crystal.
- 30 10. The article of claim 9, wherein the semiconductor wire is a single crystal.

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11. The article of claim 1, wherein at least the portion of the semiconductor wire has a thickness of no more than about 200 nm.
12. The article of claim 11, wherein at least the portion of the semiconductor wire has a thickness of no more than about 100 nm.
13. The article of claim 12, wherein at least the portion of the semiconductor wire has a thickness of no more than about 50 nm.
14. The article of claim 1, wherein the semiconductor wire has an aspect ratio of at least about 2000.
15. The article of claim 14, wherein the semiconductor wire has an aspect ratio of at least about 50,000.
16. The article of claim 1, wherein at least the portion of the semiconductor wire has a diameter that has a maximum variation of no more than about 100% relative to the average diameter of the semiconductor wire.
17. The article of claim 16, wherein at least the portion of the semiconductor wire has a diameter that has a maximum variation of no more than about 20% relative to the average diameter of the semiconductor wire.
18. The article of claim 17, wherein at least the portion of the semiconductor wire has a diameter that has a maximum variation of no more than about 10% relative to the average diameter of the semiconductor wire.
19. The article of claim 18, wherein at least the portion of the semiconductor wire has a diameter that has a maximum variation of no more than about 5% relative to the average diameter of the semiconductor wire.

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20. The article of claim 1, wherein at least the portion of the semiconductor wire has a diameter that has a maximum variation of no more than about 100 nm relative to the average diameter of the semiconductor wire.
- 5 21. The article of claim 20, wherein at least the portion of the semiconductor wire has a diameter that has a maximum variation of no more than about 10 nm relative to the average diameter of the semiconductor wire.
22. The article of claim 21, wherein at least the portion of the semiconductor wire has
10 a diameter that has a maximum variation of no more than about 5 nm relative to the average diameter of the semiconductor wire.
23. The article of claim 22, wherein at least the portion of the semiconductor wire has
15 a diameter that has a maximum variation of no more than about 3 nm relative to the average diameter of the semiconductor wire.
24. The article of claim 1, wherein the semiconductor wire includes a length of at least about 1 mm and a thickness of no more than about 500 nm, and no more than about 1 grain boundary per micrometer of semiconductor wire.
20
25. An article, comprising:
a semiconductor wire having an aspect ratio of at least about 2000 and no more than 1 grain boundary per micrometer of semiconductor wire.
- 25 26. The article of claim 25, wherein the wire has a length of at least about 0.3 mm.
27. The article of claim 26, wherein the wire has a length of at least about 0.5 mm.
28. The article of claim 27, wherein the wire has a length of at least about 1 mm.
30
29. The article of claim 25, wherein the semiconductor wire comprises silicon.

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30. The article of claim 25, wherein the semiconductor wire consists essentially of silicon.
31. The article of claim 25, wherein the semiconductor wire is a single crystal.
- 5 32. The article of claim 25, wherein the semiconductor wire has a thickness of no more than about 500 nm.
- 10 33. The article of claim 25, wherein the semiconductor wire has an aspect ratio of at least about 50,000.
34. The article of claim 33, wherein the semiconductor wire has an aspect ratio of at least about 100,000.
- 15 35. The article of claim 34, wherein the semiconductor wire has an aspect ratio of at least about 200,000.
36. The article of claim 25, wherein the semiconductor wire has a diameter that has a maximum variation of no more than about 100% relative to the average diameter of the semiconductor wire.
- 20 37. The article of claim 36, wherein the semiconductor wire has a diameter that has a maximum variation of no more than about 20% relative to the average diameter of the semiconductor wire.
- 25 38. The article of claim 25, wherein the semiconductor wire has a diameter that has a maximum variation of no more than about 100 nm relative to the average diameter of the semiconductor wire.
- 30 39. The article of claim 38, wherein the semiconductor wire has a diameter that has a maximum variation of no more than about 10 nm relative to the average diameter of the semiconductor wire.

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40. A method, comprising:
growing a semiconductor wire from a nanoparticle using chemical vapor deposition by exposing the nanoparticle to Si_2H_6 .
- 5 41. The method of claim 40, wherein the semiconductor wire is at least about 10 micrometers in length.
42. The method of claim 41, wherein the semiconductor wire is at least about 100 micrometers in length.
- 10 43. The method of claim 42, wherein the semiconductor wire is at least about 1 mm in length.
44. A method, comprising:
15 growing a semiconductor wire from a nanoparticle using chemical vapor deposition at a temperature of between about 300 °C and about 500 °C.
45. The method of claim 44, wherein the temperature is between about 370 °C and about 410 °C.
- 20 46. The method of claim 44, wherein the semiconductor wire is at least about 10 micrometers in length.
47. The method of claim 46, wherein the semiconductor wire is at least about 100 micrometers in length.
- 25 48. The method of claim 47, wherein the semiconductor wire is at least about 1 mm in length.
- 30 49. An article, comprising:
at least 50 transistors, diodes, sensors, memories, and/or photovoltaic cells each comprising a common nanoscale wire.

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50. An article, comprising:
at least 50 transistors, diodes, sensors, memories, and/or photovoltaic cells
each comprising a common wire having no more than 1 grain boundary per
micrometer of common wire.

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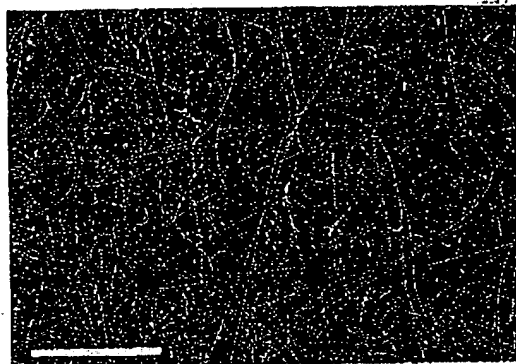


Fig. 1A

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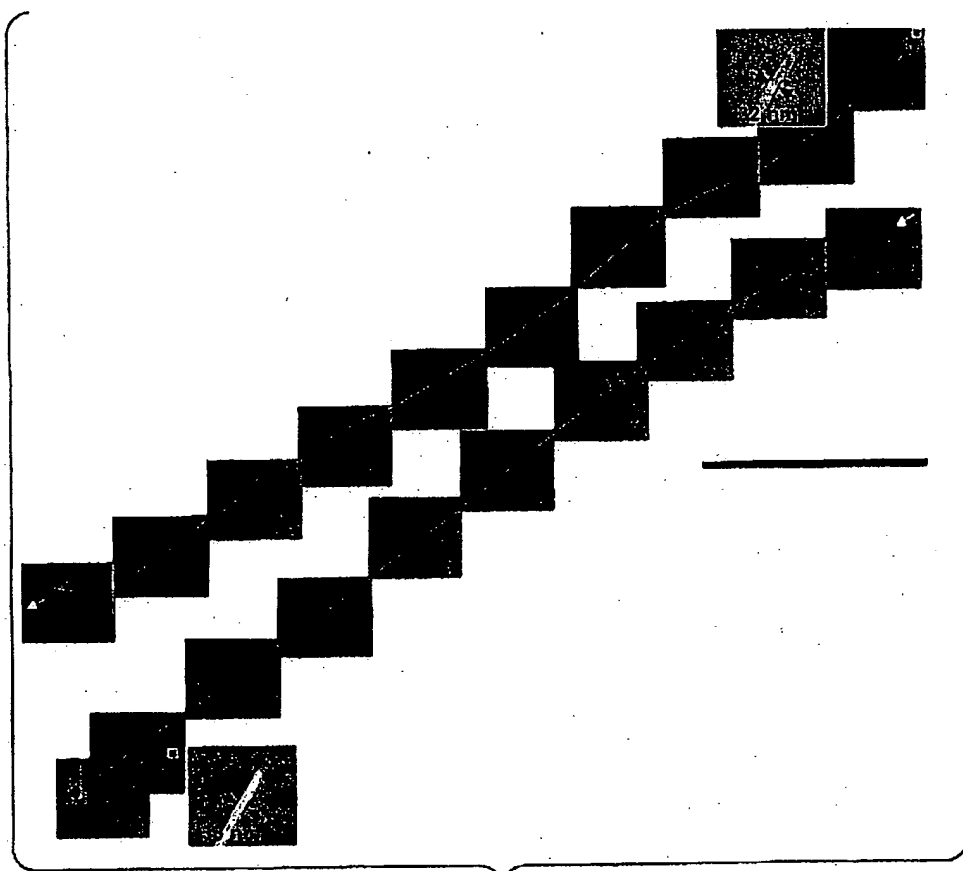


Fig. 1B

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Fig. 1C

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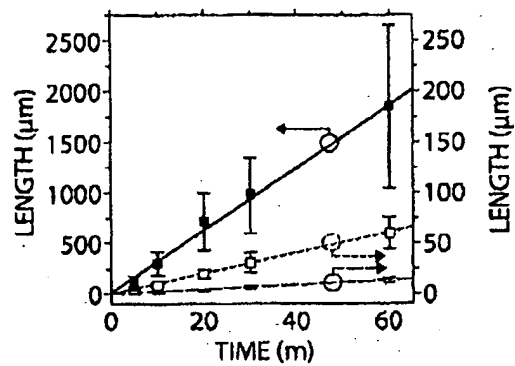


Fig. 2A

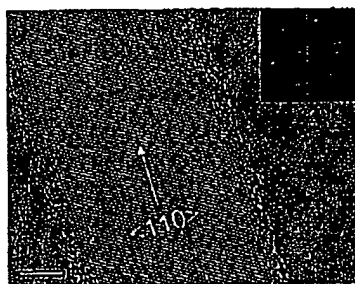


Fig. 2B

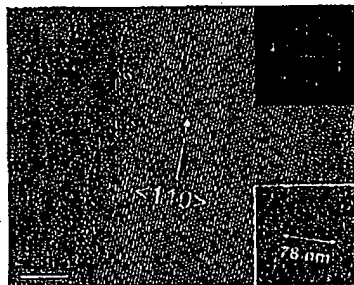


Fig. 2C

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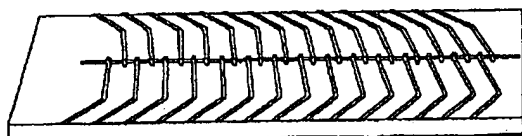


Fig. 3A

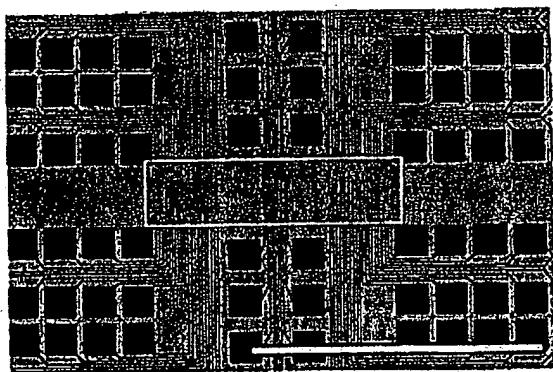


Fig. 3B

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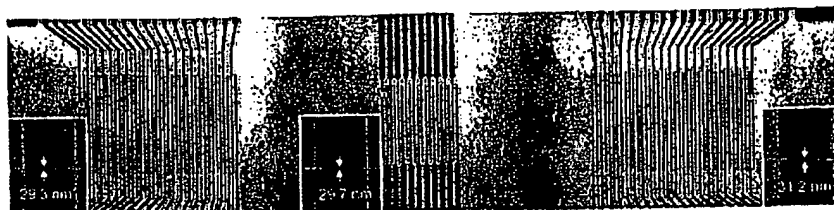


Fig. 3C



Fig. 3D

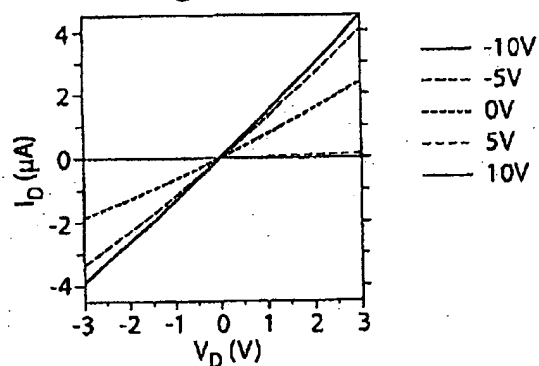


Fig. 3E

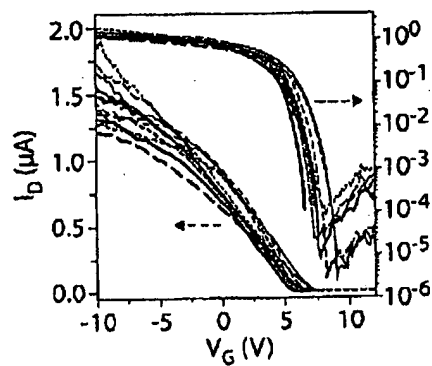


Fig. 3F

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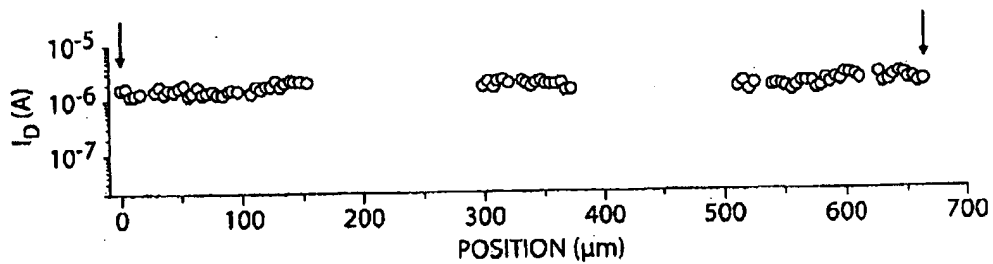


Fig. 3G

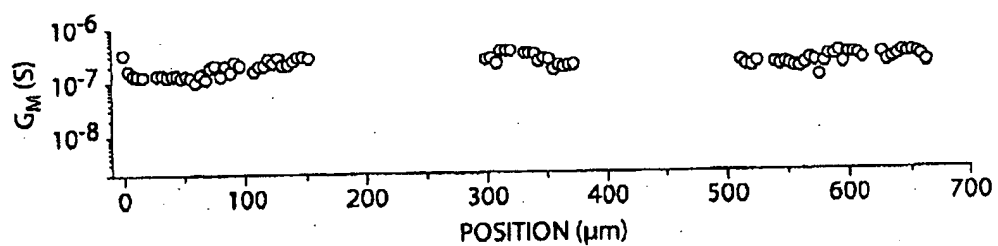


Fig. 3H

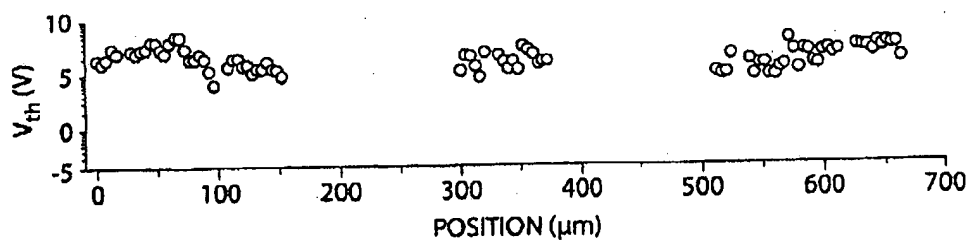


Fig. 3I

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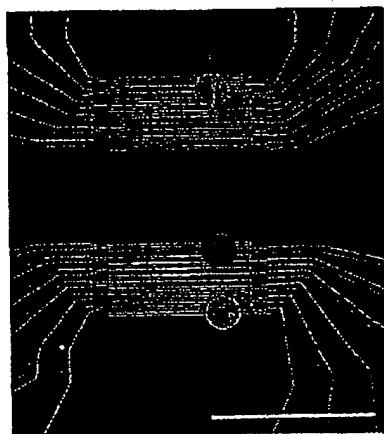


Fig. 4A

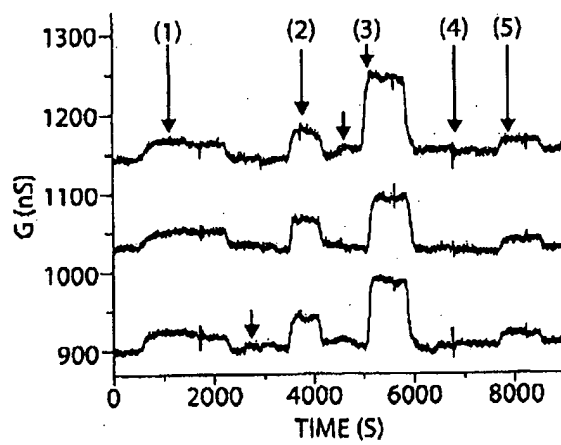


Fig. 4B